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Neutron Scattering to Characterize Cu/Mg(Li) Destabilized Hydrogen Storage Materials

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ABSTRACT

Cu-Li-Mg-(H,D) was studied as an example of destabilizer of the Ti-(H,D) system. A Cu-Li-Mg alloy was prepared resulting in the formation of a system with 60.5 at% of $CuLi_{0.08}Mg_{1.92}$, 23.9 at% of $CuMg_2$ and 15.6 at% of Cu_2Mg. Titanium was added to a fraction of this mixture so that 68.2 at% (47.3 wt%) of the final mixture was Ti. The mixture was ground and kept at 200 °C/473 K for 7h under H_2 or 9h under D_2 at P = 34 bar. Under those conditions, neutron powder diffraction shows the formation of TiD_2, as well as of the deuteride of $CuLi_{0.08}Mg_{1.92}$. Similarly inelastic neutron scattering shows that at 10 K TiH_2 is present in the sample, together with the hydride of $CuLi_{0.08}Mg_{1.92}$. Interestingly, at 10 K TiH_2 is very clearly detected and at 300 K TiH_2 is still clearly present as indicated by the neutron vibrational spectrum, but $CuLi_{0.08}Mg_{1.92}$-H is not detected anymore. These results indicate that $Ti(H,D)_2$ is possibly formed by diffusion of hydrogen from the Cu-Li-Mg-(H,D) alloys. This is an intriguing result since TiH_2 is normally synthesized from the metal at T > 400°C/673 K (and most commonly at T ~ 700 °C/973 K). In the presence of $CuLi_{0.08}Mg_{1.92}$, TiH_2 forms at a temperature that is 300 – 400 K lower than that needed to synthesize it just from the elements.

INTRODUCTION

The pioneering work of Reilly and Wiswall [1] on hydrogen storage in $CuMg_2$ provides the first clear example of destabilization. $CuMg_2$ was reversibly hydrogenated to $3/2MgH_2 + 1/2Cu_2Mg$ with an equilibrium pressure of 1 bar at 240 °C/513 K. This temperature is ~ 40 K lower than T(1 bar) for pure MgH_2. However, since $CuMg_2$ does not form a hydride, this work was set aside until very recently.

The current search for an on-board hydrogen storage material has led to a point where only a system of 4 elements will cover all specifications and this with difficulty. A destabilization strategy then becomes a viable, attractive path forward for further progress.

$CuMg_2$ has an orthorhombic crystal structure (Fddd). However $CuLi_xMg_{2-x}$ (x = 0.08) has a hexagonal crystal structure ($P6_222$), just like $NiMg_2$ - a compound known for its hydrogen storage properties. $NiMg_2$ absorbs up to 3.6 wt% of hydrogen, at 1 bar and 282 °C/555 K. In spite of the fact that the percentage of H_2 absorbed by $NiMg_2$ is enough to propitiate practical applications, the temperature at which the alloy desorbs hydrogen is much too high for current applications. Still, the alloy can be found in practical applications when added to other elements/alloys. A comparison between the phase diagrams of the systems Cu-Mg and Ni-Mg shows that these binary systems form compounds with similar stoichiometry. $NiMg_2$ is formed by peritectic reaction of the elements at 759 °C/1032 K and $CuMg_2$ at 568 °C/841 K by

congruent melting. The presence of Li lowers even further the melting point of $CuMg_2$. Since the energy of formation of the hydride is related to that of the primary alloy, it was hypothesized that $CuLi_xMg_{2-x}$ might also be a hydrogen storage material similar to $NiMg_2$. Presumably, its advantage would be that it would release hydrogen at a lower temperature (possibly close to room temperature). Preliminary studies at the Manuel Lujan, Jr. Neutron Scattering Center showed that $CuLi_xMg_{2-x}$ absorbs 5.3 wt% H at an equilibrium pressure of approx. 27 bar at 200 °C/473 K. DSC/TG experiments show that a considerable amount of hydrogen can be released at T < 100 °C/373 K. If these results are confirmed, this will mean that, not only $CuLi_xMg_{2-x}$ absorbs a considerable amount of hydrogen, but also will probably release it at a temperature in the range of 50 °C /323 K to 200 °C/473 K, where applications are easier to develop. Hence it should be possible to use this alloy with fuel cells or in batteries. It was also observed that a sample containing $CuMg_2$ could release hydrogen at 180 °C/453 K ≤ T ≤ 210 °C/483 K, probably meaning that the presence of $CuLi_xMg_{2-x}$ will make MgH_2 releasing hydrogen at an even lower temperature. In this work we have characterized Cu-Li-Mg+Ti+(H,D) hydrogen storage systems and its thermodynamic properties by means of neutron scattering and other complementary techniques.

EXPERIMENT

An alloy of the system Cu-Li-Mg was prepared by melting the elements together: Cu (electrolytic, 99.99% purity, 325 mesh), Mg (99.8% purity, 200 mesh, Alfa Aesar), and small (less than 3mm wide) pieces of Li (99% purity, Alfa Aesar), at 850 °C/1123 K for 1h using a stirring device. The alloy was quenched into liquid nitrogen. The resulting samples had 60.5 at% of $CuLi_{0.08}Mg_{1.92}$, 23.9 at% of $CuMg_2$ and 15.6 at% of Cu_2Mg. The samples were first characterized by means of XRD using a Rigaku Ultima III powder diffractometer, and their composition was roughly determined by means of the Match software, [2] which uses the "Reference Intensity Ratio method" RiR - method) [3] to obtain phase fractions. Patterns were collected with CuKα typically from 2θ = 15 to 70º with steps of 0.02º and a counting time of 10 s per bin.

This brittle material was mixed with Ti (99.9% purity, 325 mesh, Alfa Aesar) so that 68.2 at%/47.3 wt% of the final mixture was Ti. The mixture was ball-milled for 3 h in a dry box under a He protective atmosphere. Part of the resulting mixture was then divided into two portions and each of them was sealed inside a stainless steel crucible and kept at 200 °C for 7h under H_2 or 9h under D_2 both at P = 34 bar. These samples were then cooled to 5 K (HIPD, neutron powder diffraction) and 10 K (FDS, neutron vibrational spectroscopy) over a period of 2 to 3 hours. Differential Scanning Calorimetry (DSC) / Thermo Gravimetric (TG) measurements were performed under Ar with a Netzsch instrument (STA 449C) from room temperature to 450 °C/723 K, using alumina pans and lids and different heating rates (5 and 10 °C/min.).

Time-of-flight (TOF) neutron diffraction data were collected on the neutron powder diffractometer (HIPD) at the Manuel Lujan, Jr. Neutron Scattering Center at Los Alamos National Laboratory. We have measured a sample containing Cu-Li-Mg-Ti-D at 5 K, 60 K, 100 K, 200 K and 300 K for 8 h / each. The structural data were refined using GSAS [4]. Since there were up to five phases to refine, and since all the phases have well defined structural parameters at all temperatures [5], except the deuteride of $CuLi_{0.08}Mg_{1.92}$ whose structural parameters and stoichiometric composition are not well established yet, but were, nevertheless, Rietveld refined

in a previous work [6] (Fig. 1), we have used the Model-biased method [4] for all phases except TiD_2 (tetragonal and cubic) [7,8] for which Rietveld refinement was used in the last step to confirm results.

The Filter Difference Spectrometer (FDS) was used for neutron vibrational spectroscopy. We have analyzed, at 10 K, samples in the systems Cu-Li-Mg, Cu-Li-Mg-H, Cu-Li-Mg-Ti, and Cu-Li-Mg-Ti-H. The latter was also analyzed at 300 K.

DISCUSSION

Results from neutron diffraction indicate that from 5 K to 100 K only $CuLi_{0.08}Mg_{1.92}$, $CuMg_2$, Cu_2Mg, Ti and the deuteride of $CuLi_{0.08}Mg_{1.92}$ that was refined as being monoclinic C 2/m as in previous work shown in Fig. 1 were present. At 200 K the system can be described as having the same phases that at 100 K, except for the fact that instead of Ti, there are new peaks corresponding to TiD_2 (tetragonal) (Figs. 2, 3). At 300 K, TiD_2 suffers a structural phase transition and it is no longer tetragonal but cubic (Figs. 2, 3) as reported before in the literature [7]. These results support the hypothesis that the Cu-Li-Mg system is the first phase to become deuterised. When the sample containing Cu-Li-Mg-Ti-D was quenched to 5 K, after absorbing D_2 at 200 °C/473 K, it could not be noticed the presence of any of Ti's deuteride phases but it was possible to observe the presence of the deuteride phase of $CuLi_xMg_{2-x}$ (x = 0.08). Then, it seems that by diffusion, Ti will also become deuterised above 100 K (possibly near 200 K).

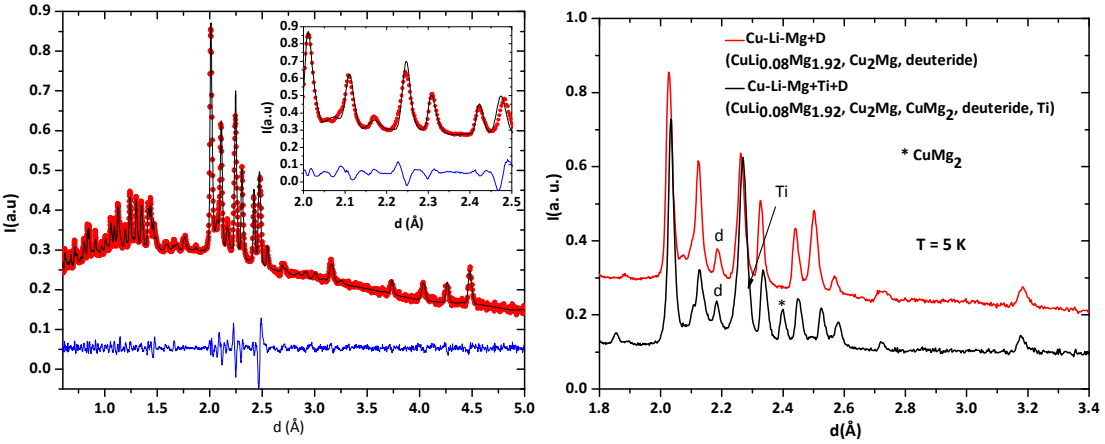

Figure 1. Diffraction pattern obtained with HIPD, at 5 K of a sample containing 75.6 at% of $CuLi_{0.08}Mg_{1.92}$, 24.4 at% of Cu_2Mg and that was deuterised at 200 °C/473 K. Rietveld refinement shows that the deuteride phase of $CuLi_{0.08}Mg_{1.92}$, $CuLi_{0.08}Mg_{1.92}D_4$, can be monoclinic C 2/m. Nevertheless, these results are still preliminary. On the right, comparison between the diffraction patterns of samples containing Cu-Li-Mg+D (the same pattern as on the left) and Cu-Li-Mg+D+Ti.

From FDS measurements, it is possible to clearly detect the presence of TiH_2 (Fig. 3 – right), since 10 K, by the presence of a peak at 1155 cm^{-1} corresponding to vibration of the H in the Ti positions, Ti-H. At this temperature it is still present the hydride phase of $CuLi_{0.08}Mg_{1.82}$ (noticed by the presence of bending modes correspondent to the peaks at around 470, 592 and 725 cm^{-1} that can be seen both on the Cu-Li-Mg-H and Cu-Li-Mg-Ti-H (10K) samples), but at

300 K, this phase cannot be seen anymore. Thus, the hypothesis about hydrogen diffusing from the Cu-Li-Mg-H system to Ti can also be supported by these measurements as well. Analyzing DSC curves, it can be inferred from Fig. 4 that after FDS measurements, there was only 0.3 wt% of mass loss from room temperature to 450 °C/723 K. Mass loss started before 100 °C/373 K, as it happens in the Cu-Li-Mg-H system, and it is probably due to hydrogen desorption from $CuLi_{0.08}Mg_{1.92}$-H. On the other hand, it cannot be seen a new rate of mass loss after approx. 200 °C/ 473 K, as it can be seen in Fig. 5 for the Cu-Mg-Li-H samples. The peak correspondent to 282 °C/555 K it is not observable in the DSC curves of Fig. 4 as well. This is probably due to the fact that instead of $CuLi_{0.08}Mg_{1.92}$-H destabilizing MgH_2 that is formed from $2CuMg_2 + 3H_2 \leftrightarrow 3MgH_2 + Cu_2Mg$, in presence of Ti, it will destabilize or act as a catalyst of Ti.

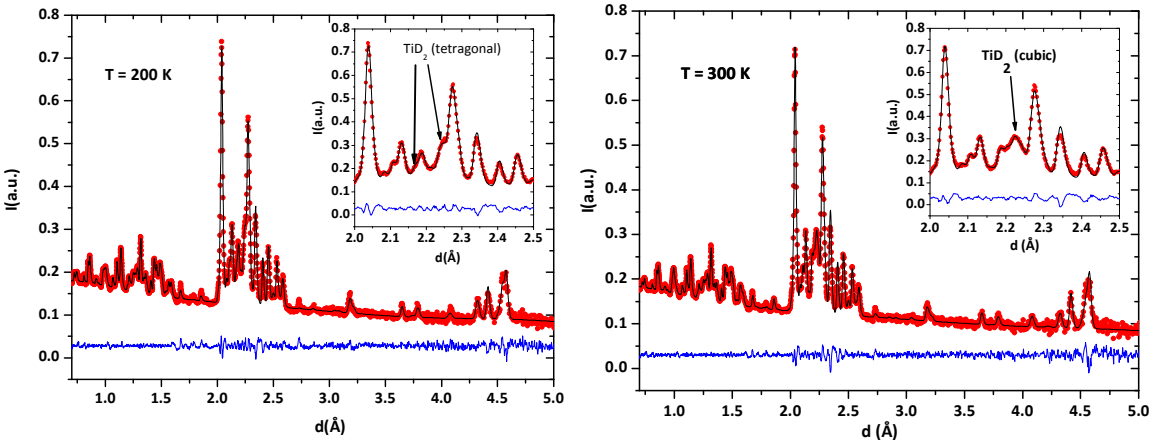

Figure 2. Diffraction patterns obtained with HIPD, at 200 K and 300 K of a sample containing 31.8 % of (60.5 at% of $CuLi_{0.08}Mg_{1.92}$, 23.9 at% of $CuMg_2$ and 15.6 at% of Cu_2Mg) + 68.2 at% of Ti and that was deuterised at 200 °C/473 K. Rietveld refinement shows the tetragonal structure of TiD_2 at 200 K and the cubic at 300 K.

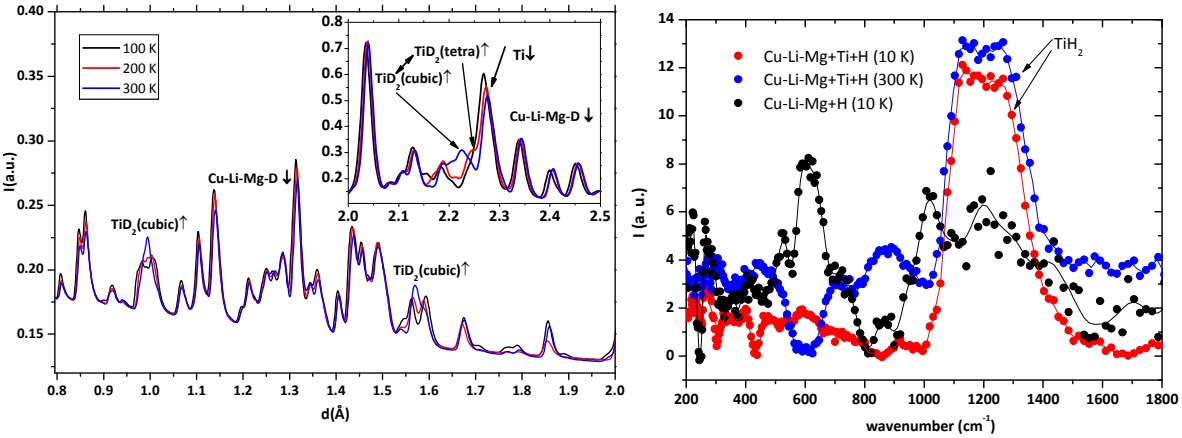

Figure 3. Diffraction patterns and inelastic spectra, obtained at FDS, of a sample containing 31.8 % of (60.5 at% of $CuLi_{0.08}Mg_{1.92}$, 23.9 at% of $CuMg_2$ and 15.6 at% of Cu_2Mg) + 68.2 at% of Ti and that was deuterised (diffraction)/hydrogenised(spectroscopy) at 200 °C/473 K. Results show the presence of TiD_2/TiH_2.

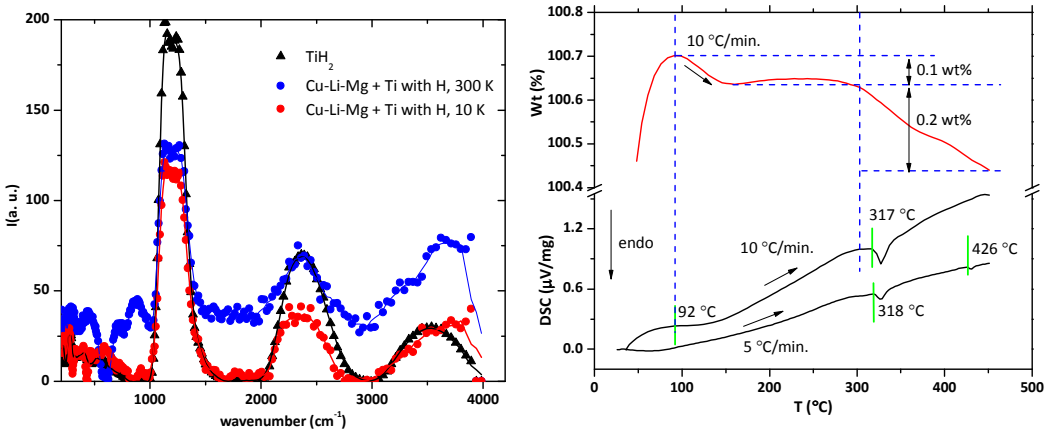

Figure 4. Inelastic spectra of a sample containing 31.8 % of (60.5 at% of $CuLi_{0.08}Mg_{1.92}$, 23.9 at% of $CuMg_2$ and 15.6 at% of Cu_2Mg) + 68.2 at% of Ti and that was hydrogenised at 200 °C/473 K in comparison with the TiH_2 spectrum. Results show the presence of TiD_2/TiH_2. DSC/TG curves of a sample containing 31.8 % of (60.5 at% of $CuLi_{0.08}Mg_{1.92}$, 23.9 at% of $CuMg_2$ and 15.6 at% of Cu_2Mg) + 68.2 at% of Ti and that was hydrogenised at 200 °C/473 K after being measured in FDS.

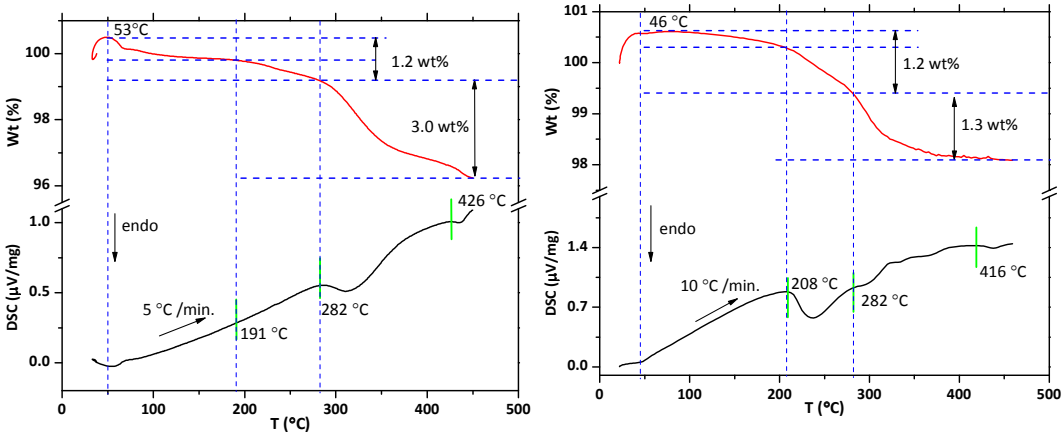

Figure 5. DSC/TG curve of a sample containing 60.5 at% of $CuLi_{0.08}Mg_{1.92}$, 23.9 at% of $CuMg_2$ and 15.6 at% of Cu_2Mg and that was hydrogenised at 200 °C/473 K and of a sample containing 64.3 at% of $CuLi_{0.08}Mg_{1.92}$, 19.6 at% of $CuMg_2$ and 16.1 at% of Cu_2Mg and that was also hydrogenised at 200 °C/473 K.

Hence, 317 °C/590 K will probably be lower limit temperature for TiH_2 to release hydrogen.

Another important support for the previous hypothesis is that neither in the neutron diffraction patterns, nor in FDS we could detect new phases. Further, at 416 °C /689 K-426 °C/699 K, there is a clear endothermic peak corresponding to the melting point of $CuLi_{0.08}Mg_{1.92}$ indicating the previous presence of this phase.

The amount of mass loss is not conclusive about the stoichiometry of the hydrides, since DSC/TG is not the suitable measurement to obtain this information, and further we did not expect that the samples were saturated with hydrogen prior to the experiment. Additionally, samples were not cycled before and the involving atmosphere was not of H_2 as it would be more

appropriate. Nonetheless, these experiments give valuable information about approximated temperatures at which the system starts to lose mass at a certain rate.
It is also possible that additionally to the mass loss effect; there will be a slightly increase of mass due to oxidation, although this effect is covered by the first.

CONCLUSIONS

We have added Ti to a system composed by Cu-Li-Mg and the mixture was hydrogenated/deuterated. Neutron scattering, XRD and DSC experiments were performed and it can be concluded that, in the presence of Ti mechanically mixed, $CuLi_{0.08}Mg_{1.92}$ will destabilize or catalyze Ti and $Ti(H,D)_2$ will be synthesized at 200 K. The latter represents a very significant decrease of temperature since $Ti(H,D)_2$ can only be synthesized from Ti at $T > 773$ K, usually at 1000 K. On the other hand, it is possible that TiH_2 will start releasing hydrogen (at 1 bar) at ~ 590 K which is also a significant decrease from 700 K - the lowest value found in the literature for the latter to occur.

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